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## Kinetic study of the oxidation by oxygen of liquid Al-Mg5% alloys

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### Keywords :

Al-Mg ; oxidation ; oxygen pressure ; kinetics ; growth reactivity ; reaction mechanism

### Abstract :

The oxidation into MgO of an industrial Al-Mg 5% alloy in the liquid state has been studied at 700°C by thermogravimetry, under controlled oxygen partial pressure. Since the kinetic curves were not reproducible, it was not possible to obtain directly from them the variations of the areic conversion rate (mole of MgO.s<sup>-1</sup>.m<sup>-2</sup>) versus the oxygen partial pressure. Therefore, it has been necessary to use a method based on the isolation method, which allowed us to overcome the problems of non-reproducibility of the curves. It was found that the areic reactivity of growth of MgO decreases when the oxygen pressure increases. A reaction mechanism in elementary steps has been proposed to account for these results, involving two competitive oxygen adsorptions on the MgO surface.

### 1. INTRODUCTION

During the elaboration of aluminium-magnesium alloys, which are widely used in industry, the surface of the liquid metal may be oxidised, mainly leading to the formation of MgO, specially in the case of alloys containing more than 3% in magnesium [1-2]. To avoid this drawback, beryllium was added to the alloys in the past. Present knowledge of this element potential hazards leads most aluminium manufacturers to discard its use in spite of the very low level involved. Anyway, it is planned to be forbidden soon. Thus, it is necessary to find alternative ways to prevent oxidation.

It is therefore important to understand the mechanisms involved in the formation of magnesium oxide from the alloy. The gaseous atmosphere involved in the industrial process is quite complex, since several gases can react with the alloys (oxygen, water vapour, nitrogen, carbon dioxide...).

So, we have studied a « simplified » system: the oxidation of an Al-Mg 5% alloy by oxygen. This article deals with an experimental study of the influence of the oxygen pressure on the oxidation, and an interpretation of the results in order to have a better knowledge of the reaction mechanism.

The transformation of a solid involves the processes of nucleation and growth of the new phase (MgO in our case). The experimental rate corresponds to the growth of MgO, thus the modelling of the transformation is reduced to the growth model. It is simplified using the following assumptions:

- (i) The system is in a quasi-steady state.
- (ii) The derivative of the fractional conversion  $\alpha$  versus time, which will be also called the rate, can be written:

$$R = \frac{d\alpha}{dt} = \Phi.E \quad \text{Eq. 1}$$

where  $\Phi$  is the areic « growth reactivity » of MgO (in  $\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ ), which depends on the physico-chemical variables (pressure P, temperature T, magnesium activity...), and E is the « space function » ( $\text{m}^2\cdot\text{mol}^{-1}$ ), characteristic of the extent of the area where the rate-limiting step of the growth occurs. E depends on the time and on the history of the solid from the beginning of the transformation up to the considered instant [3]. These two assumptions can be verified experimentally [3-5].

Then, an experimental method, based on the isolation method [6,7], can be used to obtain directly the variations of  $\Phi$  with the physico-chemical variables (particularly the oxygen pressure).

In this article we present first the results of the kinetic study of the oxidation of an Al-Mg alloy into MgO; then a mechanism is proposed in order to account for the experimental results on the variations of the areic growth reactivity with oxygen pressure.

## 2. EXPERIMENTAL

The alloy is an industrial Al-Mg 5% alloy, supplied by Pechiney (purity about 99%). The samples are cylinders of 1mm height and 9mm diameter. Before each experiment, they were manually polished with grade 500 SiC paper and rinsed with acetone (the polishing method of the samples has no influence on the kinetic curves).

The oxidation of the liquid alloy was followed by isothermal thermogravimetry at 700°C (thermobalance SETARAM TAG 24). The experiments were carried out at atmospheric pressure, under a flowing mixture of helium and oxygen ( $1\text{l}\cdot\text{h}^{-1}$ ), the partial pressures being controlled by mass-flowmeters (Brooks 5850E). The heating of the samples was carried out under oxygen at atmospheric pressure since it has been observed that a high oxygen pressure allows to limit the oxidation of the liquid alloy; the oxygen pressure chosen for the experiment is established after 30 minutes of isotherm at 700°C.

The experiments of simultaneous calorimetry and thermogravimetry were performed using a SETARAM TG-DSC 111, under a flowing mixture of helium and oxygen.

## 3. RESULTS

### 3.1. Kinetic curves

As shown in previous studies [8-12], for alloys containing more than 3% in magnesium, MgO is the first phase which appears during the oxidation, up to 1.7% of weight increase. Above 1.7% (corresponding to a residual magnesium activity lower than 0.023),  $\text{MgAl}_2\text{O}_4$  is the thermodynamically stable phase, its formation was confirmed by X-Ray diffraction [12]. Consequently, the kinetic curves will be limited to a weight increase of about 1.7%.

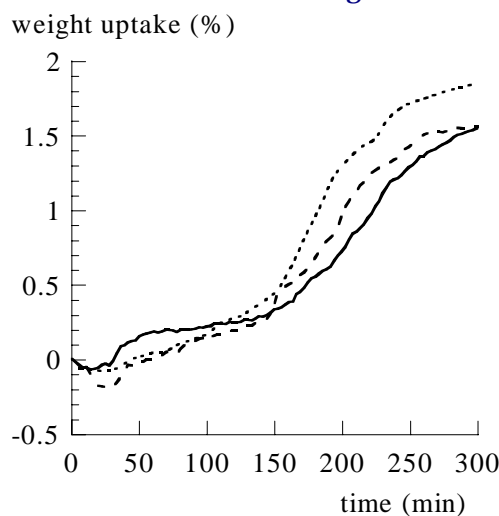


Figure 1 : Curves of weight gain and non reproducibility ( $T=700^\circ\text{C}$ ,  $P_{\text{O}_2}=400\text{ hPa}$ ).

During the oxidation experiments, a thin solid MgO layer is formed when the temperature increases, and when the alloy melts, at about 648°C, it remains inside this solid layer which envelops the liquid metal. This layer undergoes strong deformations during the experiments, it is very rough and irregular. SEM observations [13] have shown that it appears quite different from one experiment to another, even for samples oxidised up to the same weight uptake, in the same conditions of temperature and pressure.

It has also been seen that the oxide layer is formed of small MgO particles (about 0.5 µm); moreover, some holes are observed inside the samples, in which MgO parallelepipeds are located (10 to 15 µm).

The oxidation experiments have been carried out with oxygen pressures ranging from 200hPa to 800hPa. The various kinetic curves have the shape given in Fig. 1 (corresponding to an oxygen pressure of 400hPa): the curves are very irregular and not reproducible, which is not surprising since the samples undergo very important morphological changes during the reaction, which differ from an experiment to another.

### 3.2. Steady state assumption.

It can be shown [4] that when a system is in a steady state, there must be an affinity relationship between the curves of reaction rate versus time, obtained with two different experimental techniques, the axis being the rate axis and the direction the time axis.

We have chosen to measure simultaneously the oxidation rate by thermogravimetry and calorimetry (heat flow). The curves of rate of weight uptake and heat flow versus time have to be superimposed in two axis systems with different ordinate scales. Fig. 2 shows the curves obtained at 700°C for an oxygen pressure of 200hPa.

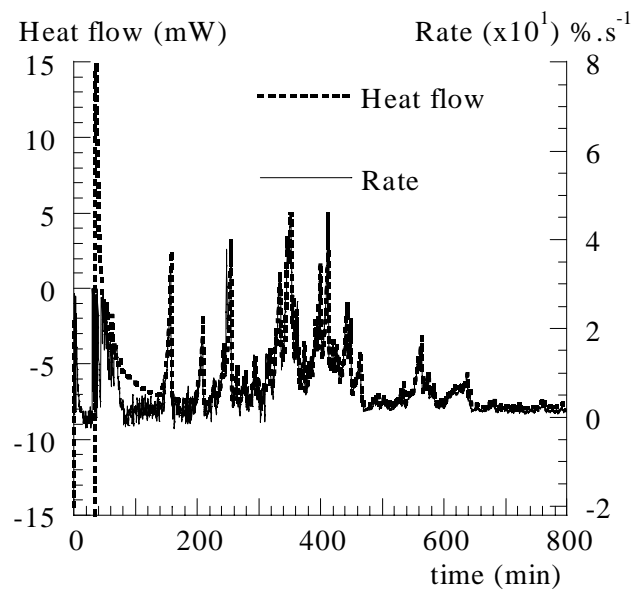


Figure 2: Steady state test  $\Phi E$  (700°C,  $P_{O_2}=200$  hPa)

During the temperature increase (10°C/min), the alloy melting (at about 648°C) induces a strong endothermic signal, which hides the exothermic signal due to the oxidation up to about 80 minutes (or  $\Delta m=0.4\%$ ). Then, the curves are very well superimposed. Thus, the approximation of the steady state is valid at least from a weight uptake of 0.4%, *i.e.* a fractional conversion equal to 0.12.

### 3.3. « $\Phi E$ » assumption

In order to verify that the rate  $R$  can be written as in Eq. 1, we use the isolation method, which consists into changing suddenly a physico-chemical variable ( $P$ ,  $T$ ) from a value  $Y_0$  to a value  $Y_1$ , at a given fractional conversion. Practically, we have changed the oxygen pressure from

400hPa to 200hPa, at various fractional conversions. Some experimental curves are given in Fig. 3a, the pressure changes being indicated by the horizontal arrows.

Let  $R_{bi}(P_0, \alpha_i)$  and  $R_{ai}(P_1, \alpha_i)$  be the rates before and after the pressure change at the fractional conversion  $\alpha_i$ , they can be written (cf. Eq. 1) :

$$R_{bi}(P_0, \alpha_i) = \Phi(P_0) E(\alpha_i) \quad \text{and} \quad R_{ai}(P_1, \alpha_i) = \Phi(P_1) E(\alpha_i)$$

so, their ratio is :

$$\frac{R_{ai}(P_1, \alpha_i)}{R_{bi}(P_0, \alpha_i)} = \frac{\Phi(P_1)E(\alpha_i)}{\Phi(P_0)E(\alpha_i)} = \frac{\Phi(P_1)}{\Phi(P_0)} \quad \text{Eq. 2}$$

The ratio of the rates before and after the pressure change does not depend on the fractional conversion: thus, the « $\Phi E$ » assumption is verified if this ratio is constant, whatever the fractional conversion at which the pressure is changed is.

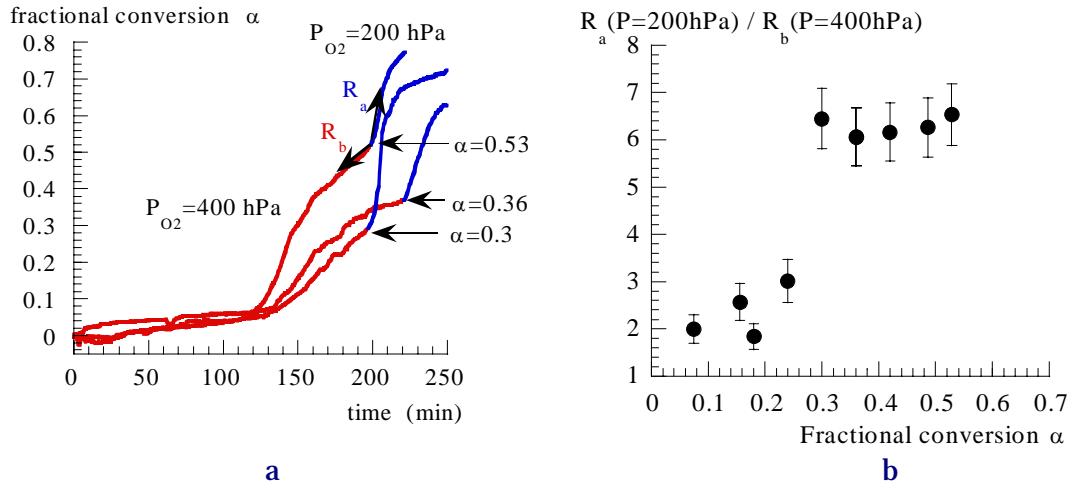


Figure 3: (a) application of the isolation method to the « $\Phi E$ » test : oxygen pressure changes (400hPa to 200 hPa) at various fractional conversions, and (b) results of the test.

The results are indicated in Fig. 3b, which shows that two domains of weight uptake can be distinguished in which the « $\Phi E$ » test is verified: the rate ratio is approximately constant for a fractional conversion between 0 and 0.2 (weight uptake between 0.25% and 0.6%), and then between 0.3 and 0.52 (weight uptake between 1 and 1.7%), but the ratio value is different in each domain.

Besides, it has been verified that when the experiments are repeated several times at a given fractional conversion, the value of the rates ratio is nearly the same (error less than 10%). Thus, the reactivity  $\Phi$  (which is an intrinsic characteristic of MgO) is reproducible, the non-reproducibility of the kinetic curves (Fig. 1) coming from the irregular variations of the space function  $E$ .

Moreover, it must be noticed that the magnesium activity  $a_{Mg}$  in the alloy varies during the oxidation reaction, so the fact that the « $\Phi E$ » test is verified implies that the ratio  $R_{ai}/R_{bi}$  does not depend on  $a_{Mg}$  in each domain of weight uptake : thus, either is independent on  $a_{Mg}$ , or  $\Phi$  can be written as:

$$\Phi(T, P, a_{Mg}) = f(a_{Mg}) \cdot g(P, T) \quad \text{Eq. 3}$$

i.e.  $a_{Mg}$  is a separable variable from the growth reactivity.

### 3.4. Variations of $\Phi$ with $P_{O_2}$ in each domain of weight uptake.

The experimental method to obtain the variations of  $\Phi$  with  $P_{O_2}$  is also based on the isolation method : in that case, several changes are carried out at a given fractional conversion  $\alpha_i$ , from an oxygen pressure  $P_0$  (here 200hPa) to various pressures  $P_i$  (the temperature being constant).

The ratio of the rates before and after the change, equal to  $\Phi(P_i) / \Phi(P_0)$  according to Eq. 2, is proportional to the variations of  $\Phi$  with  $P_{O_2}$ , ( $\Phi(P_0)$  keeping the same value in all the experiments).

The variations of  $\Phi$  with  $P_{O_2}$  were obtained by changing the oxygen pressure at a fractional conversion 0.15 in the first domain of weight uptake ( $\Delta m < 0.6\%$ ) and at 0.4 in the second domain of weight uptake ( $1\% < \Delta m < 1.7\%$ ). The Fig. 4a and 4b show that in each domain, the growth reactivity decreases strongly when the oxygen pressure increases, which is quite unusual for oxidation reactions. As it can be seen, the highest the oxygen pressure, the slowest the rate, which justifies our choice of heating the samples under an oxygen pressure of one atmosphere before establishing the oxidation conditions at 700°C.

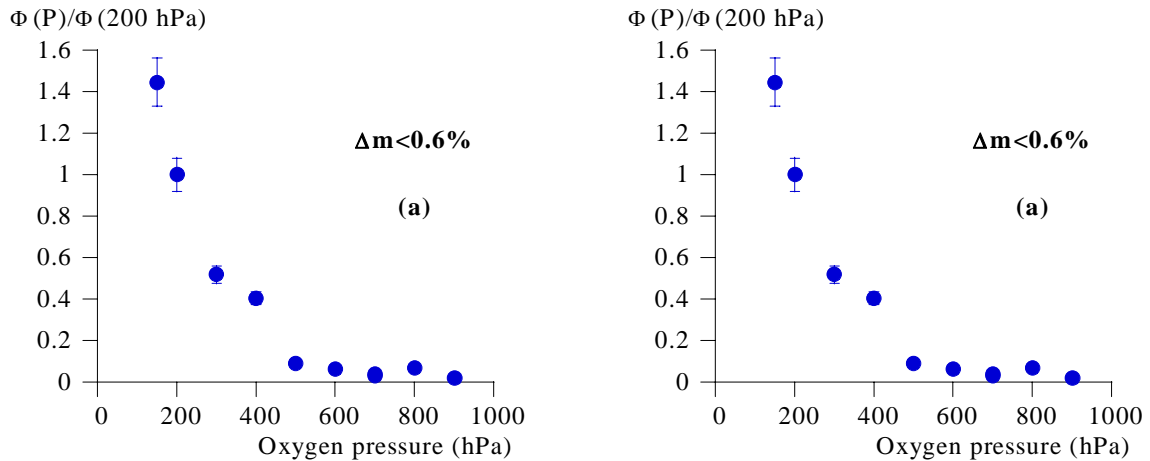


Figure 4: Variations of the growth reactivity  $\Phi$  with oxygen pressure in each domain of weight gain.

#### 4. INTERPRETATION OF THE VARIATIONS OF $\Phi$ WITH $P_{O_2}$ : GROWTH MECHANISM.

We have verified the assumption of steady state, and that the oxidation rate could be written as a product « $\Phi E$ ». These results are important to find the elementary steps of the growth mechanism, because they mean that it will be possible to use the assumption of the rate-limiting step to calculate the corresponding possible rate laws. Comparing these laws to the experimental variations of  $\Phi$  with  $P_{O_2}$  (Fig. 4) will normally lead us to determine the rate-limiting step of the reaction and thus the appropriate rate law for  $\Phi$ . Before detailing the elementary steps proposed for the reaction mechanism, a qualitative description can be attempted.

Usually, the mechanisms proposed to describe the oxidation of metals lead to an areic growth reactivity  $\Phi$  which increases when the oxygen pressure increases [12, 14-15]. Nevertheless, studying the oxidation of solid magnesium into MgO [12], we have obtained complex variations of the growth reactivity  $\Phi$  with the oxygen pressure: they were not monotonous. We have succeeded in interpreting these results considering a growth mechanism which involves two kinds of oxygen adsorption on the MgO surface [4, 16].

In the case of the alloy, we can also make this assumption to account for the inhibiting effect of oxygen on the growth reactivity of MgO, since it is well known that oxygen adsorption on oxides surface may lead to various oxygen species [17]. In the case of magnesium oxide, several oxygen adsorbed species have already been observed [18, 19], like  $O^-$  and  $O^{2-}$  species. In-situ infra-red experiments (detailed elsewhere [13, 20]), carried out during the oxidation of solid magnesium up to 500°C, have allowed to confirm the existence of adsorbed species at MgO surface, supposed to be  $O^{2-}$  species [20]. These  $O^{2-}$  species are very stable, since they are not modified at 500°C even when oxygen is removed from the gaseous atmosphere, which is in agreement with the literature data [21].



These species are supposed to be inactive for the oxidation reaction, and to occupy adsorption sites. A competitive oxygen adsorption is assumed to occur on the same sites, leading to oxygen adsorbed species which participate in the oxidation. These two kinds of adsorbed species can be described as shown in Fig. 5: some oxygen species may be adsorbed on a surface site (which could be a magnesium atom at the MgO surface), perpendicularly to the surface (scheme (a) in Fig. 5); the second kind of adsorbed species are parallel to the surface, the adsorption involving four surface sites (scheme (b) on Fig. 5). The choice of four sites will be discussed later.

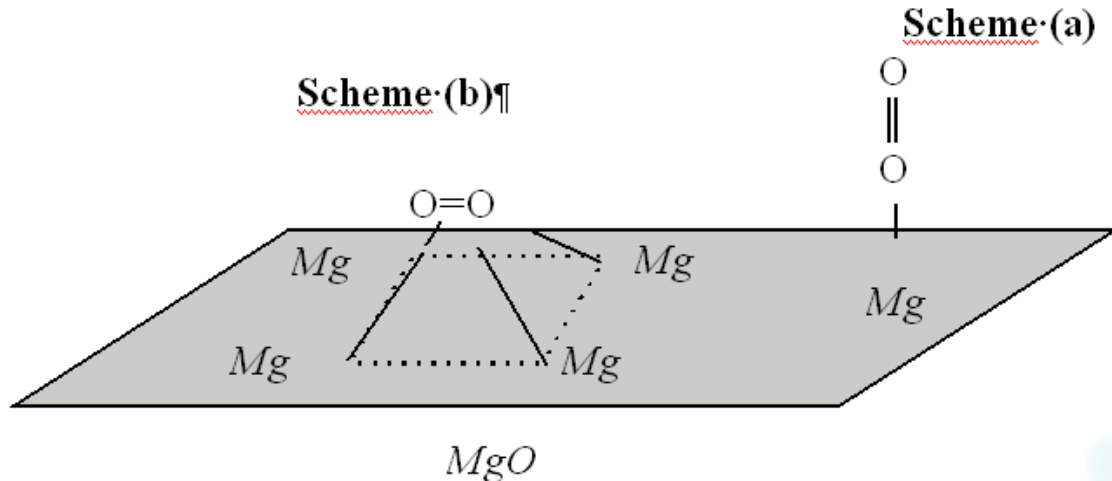


Figure 5: Schematic representation of the two kinds of adsorbed oxygen species on MgO surface.

In the following, « s » designs a surface site, which could be a magnesium atom at the MgO surface. The steps proposed for the reaction mechanism are detailed below:

- ❖ a non-dissociative adsorption:



This adsorption is considered to be at equilibrium (equilibrium constant  $K_A$ ) and the  $\text{O}_{2-\text{s}}$  species do not participate in the oxidation.

- ❖ a dissociative adsorption, in two steps, involving four sites « s »:



Then, the following steps involve the MgO point defects (magnesium vacancies and holes):

- \* step (2): external interface reaction (creation of the oxide defects)



- \* step (3): diffusion of the defects from the external interface to the internal interface

- \* step (4): internal interface reaction



A linear combination of the steps (1a), (1b), (2), (3) and (4) leads to the overall reaction:



The rate laws have been calculated using the assumption of the rate-limiting step [4]. Only the cases for which the steps of adsorption (1a), dissociation (1b) or external interface (2) are rate-

limiting lead to rate laws which can account for a decreasing rate when the oxygen pressure increases. They are indicated in Table 1.

Rate-limiting step	Growth reactivity $\Phi$
Adsorption (1a)	$\Phi = k_{1a} \frac{P_{O_2}}{\left(1 + \frac{1}{K_2 K_4 a_{Mg}} + K_A P_{O_2}\right)^4}$
Dissociation of $O_{2-s4}$ (1b)	$\Phi = k_{1b} \frac{K_{1a} P_{O_2}}{\left(1 + \frac{1}{K_2 K_4 a_{Mg}} + K_A P_{O_2}\right)^4}$
External interface reaction (2)	$\Phi = k_2 \frac{\sqrt{K_1 P_{O_2}}}{1 + \sqrt{K_1 P_{O_2}} + K_A P_{O_2}}$

Table 1: Rate laws corresponding to the rate-limiting steps (1a), (1b) and (2) ( $k_i$  and  $K_j$  are respectively the rate constants and the equilibrium constants of the steps (i) and (j)).

It can be noticed that the variation of  $\Phi$  with  $P_{O_2}$  being the same in cases (1a) and (1b), it will not be possible to choose between these two steps.

The experimental values were fitted using the functions given in Table 1 ; the results obtained for the each domain of weight uptake are shown in Fig. 6a and 6b, in the cases (1a) /or (1b) and (2) respectively.

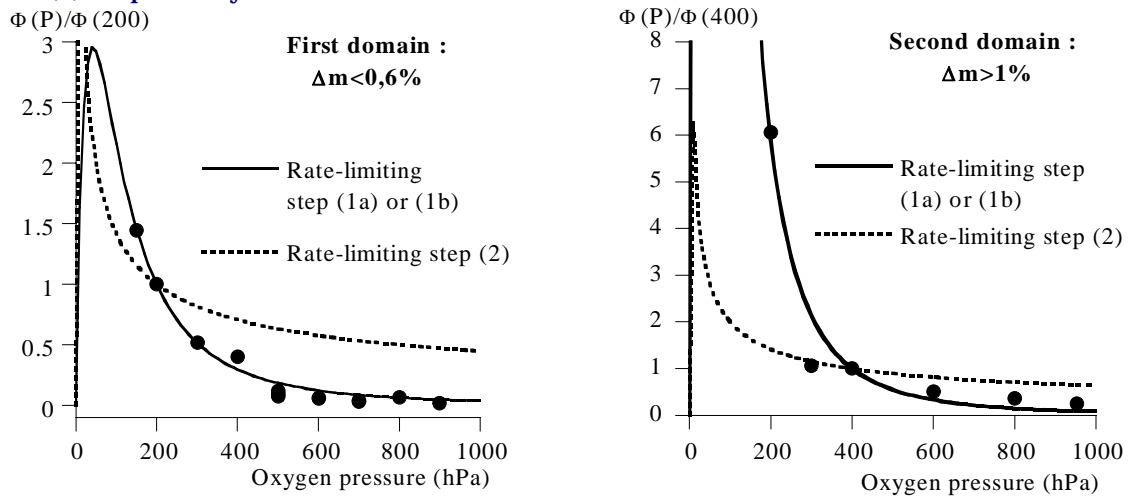


Fig. 6 : Fit between the experimental values and the theoretical rate laws in each domain of weight gain : (a) first domain,  $\Delta m < 0.6\%$ , and (b) second domain,  $\Delta m > 1\%$ .

The function corresponding to the rate-limiting step (1a) or (1b) leads to the best agreement with the experimental values, in both domains of weight gain. The step (1a) was assumed first to involve two adsorption sites instead of four, but the agreement was not as satisfactory as with four sites.

The rate law depends on the magnesium activity  $a_{Mg}$ , but the fit with the experimental values leads to a value of  $1/K_2 K_4 a_{Mg}$  of  $2.2 \cdot 10^{-2}$ , which is low compared to 1 and to  $K_A P_{O_2}$ , and thus  $\Phi$  can be considered as independent of  $a_{Mg}$ . This is compatible with the fact that the «  $\Phi E$  » test is verified (cf section 3).

The term  $1/K_2 K_4 a_{Mg}$  being neglected in the expression of the rate law,  $K_A$  (the equilibrium constant of the non-dissociative adsorption) is the only parameter to be adjusted, since in the



ratios the rate constant ( $k_{1a}$  or  $k_{1b}$ ) is eliminated. For the first and second domain of weight uptake, we obtain  $K_A=7.9$  and  $K_A=29$  respectively.

Thus, the existence of the two domains of weight uptake is linked to a change in the equilibrium constant  $K_A$ . Taking into account the two kinds of morphologies of magnesium oxide which have been observed (small grains and parallelepipeds), the two values of  $K_A$  may correspond to the oxygen adsorption on each oxide type. Thus, each domain of weight uptake is attributed to a predominant morphology.

Concerning the rate limiting step, we can not conclude whether or not it is different from one domain to another (the rate laws (1a) and (1b) being the same).

## 5. CONCLUSIONS

The oxidation kinetics of a liquid industrial Al-Mg 5% alloy has been studied according to an appropriate methodology, in order to validate a reaction mechanism. The use of the isolation method turned out to be necessary to overcome the problems due to the non-reproducibility of the kinetic curves and to obtain the variations of the areic reactivity of growth of magnesium oxide  $\Phi$  with the oxygen pressure.

It has been shown that  $\Phi$  decreases when oxygen pressure increases, which was accounted for by a mechanism involving two parallel oxygen adsorptions, one is non dissociative, the other is dissociative on four adsorption sites and participates in the oxidation. Moreover, two domains of weight uptake have been put into evidence, in which the growth reactivity  $\Phi$  is different, although the rate-limiting step seems to be the same. The origin of these two domains could not be identified with certainty, but SEM observations showing that the oxide exists under two different morphologies, and the suggested mechanism leading to distinct values of the equilibrium constant of oxygen adsorption  $K_A$  in the two domains of weight uptake, each domain could correspond to a predominant oxide morphology.

Besides, it could be interesting to determine whether the transition between the two domains (for a fractional conversion ranging from 0.2 to 0.3 for an alloy containing initially 5% in magnesium) corresponds to the formation of a given amount of magnesium oxide or to a residual magnesium content in the alloy. This could be done in a further study by using alloys with various contents in magnesium, and could lead to a better understanding of the origin of these two domains.

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